

**PROCESS FOR THE OXIDATIVE PURIFICATION OF TEREPHTHALIC
ACID**

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Cross-Reference to Related Applications

This application claims priority to U.S. Non-Provisional Application Serial No 10/315,295, filed December 9, 2002, the disclosure of which is incorporated herein by reference.

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FIELD OF INVENTION

The present invention relates to a process for the purification of a
15 crude carboxylic acid slurry. More specifically, the present invention relates to a process comprising the steps of displacing at elevated temperatures, mother liquor from a crystallized product and reslurrying the crystallized product to be separated in a solid liquid displacement zone to form a purified carboxylic acid slurry.

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BACKGROUND OF THE INVENTION:

Terephthalic acid is commercially produced by oxidation of paraxylene in the presence of a catalyst, such as, for example, Co, Mn, Br
25 and a solvent. Terephthalic acid used in the production of polyester fibers,

films, and resins must be further treated to remove impurities present due to the oxidation of para-xylene. Typical commercial process produce a crude terephthalic acid then dissolve the solid crude terephthalic acid in water at high temperatures and pressures, hydrogenating the resultant solution,
5 cooling and crystallizing the terephthalic acid product out of solution, and separating the solid terephthalic product from the liquid as discussed in U. S. Patent No. 3,584,039 herein incorporated by reference.

In many processes colored impurities from the benzil, and fluorenone families are hydrogenated to colorless products and leave the process with
10 the terephthalic acid solid product and wastewater streams. However, this invention provides an attractive process to produce a purified carboxylic acid slurry by utilizing a solid liquid displacement zone comprising a solid liquid separator at elevated temperatures after oxidation of a crude carboxylic acid slurry product and prior to final filtration and drying.

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SUMMARY OF THE INVENTION

In one embodiment of the invention, a process to produce the purified carboxylic acid slurry is provided without the use of hydrogenation
20 of the terephthalic acid or a process separating impurities from oxidation solvent as disclosed in US 3,584,039. Another example of a process for separating impurities from oxidation solvent is US 4,356,319.

In another embodiment of this invention, a process to produce a purified carboxylic acid slurry, the process comprising removing impurities from a crystallized product in a solid liquid displacement zone to form the purified carboxylic acid slurry; wherein the purified carboxylic acid slurry has
5 a b* of less than 3.5; wherein the purified carboxylic acid slurry is formed without a hydrogenation step.

In another embodiment of this invention, a process to purify a staged oxidation product the process comprising removing impurities from the staged oxidation product in a solid liquid displacement zone to form a
10 purified staged oxidation product; wherein the purified staged oxidation product has a b* of less than 3.5; wherein the purified staged oxidation product is formed without a hydrogenation step.

In another embodiment of this invention, a process to produce a purified carboxylic acid slurry is provided. The process comprises removing
15 in a solid liquid displacement zone impurities from a crystallized product to form the purified carboxylic acid slurry; wherein the solid liquid displacement zone comprises a solid liquid separator that is operated at a temperature between about 140 °C to about 160 °C; wherein the solid liquid separator is operated in a continuous mode; and wherein the solid liquid
20 separator is operated at a pressure of less than about 70 psia.

In another embodiment of this invention, a process to produce a purified carboxylic acid slurry is provided. The process comprising:

- (a) optionally, removing impurities from a crude carboxylic acid slurry in an optional solid liquid displacement zone to form a slurry product;
 - (b) oxidizing the slurry product or the crude carboxylic acid slurry in a staged oxidation zone to form a staged oxidation product;
- 5 (c) crystallizing the staged oxidation product in a crystallization zone to form a crystallized product; and
- (d) removing in a second solid liquid displacement zone impurities from the crystallized product to form the purified carboxylic acid slurry.
- 10 In yet another embodiment of this invention, a process to produce a purified carboxylic acid slurry is provided. The process comprises:
- (a) optionally, removing impurities from a crude carboxylic acid slurry in an optional solid liquid displacement zone to form a slurry product;
 - (b) oxidizing the slurry product or the crude carboxylic acid slurry in a staged oxidation zone to form a staged oxidation product;
- 15 (c) removing in a solid liquid displacement zone impurities from the staged oxidation product to form a purified staged oxidation product; and
- (d) crystallizing the purified staged oxidation product in a crystallization zone to form the purified carboxylic acid product.

20 These objects, and other objects, will become more apparent to others with ordinary skill in the art after reading this disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic of the inventive process for the oxidative purification of carboxylic acid wherein a liquid displacement zone is utilized after the crystallization zone.

Figure 2 is a schematic of the inventive process for the oxidative purification of carboxylic acid wherein a liquid displacement zone is utilized after the staged oxidation zone.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for the purification of a crude carboxylic acid slurry. The process comprises the steps of displacing at elevated temperatures mother liquor from a crystallized product and reslurrying the crystallized product in a solid liquid displacement zone to form a purified carboxylic acid slurry.

Crude terephthalic acid is conventionally made via the liquid phase air oxidation of paraxylene in the presence of a suitable oxidation catalyst. Suitable catalysts comprises at least one selected from, but are not limited to, cobalt, bromine and manganese compounds, which are soluble in the selected solvent. Suitable solvents include, but are not limited to, aliphatic mono-carboxylic acids, preferably containing 2 to 6 carbon atoms, or benzoic acid and mixtures thereof and mixtures of these compounds with

water. Preferably the solvent is acetic acid mixed with water, in a ratio of about 5:1 to about 25:1, preferably between about 8:1 and about 20:1. Throughout the specification acetic acid will be referred to as the solvent. However, it should be appreciated that other suitable solvents, such as 5 those disclosed herein, may also be utilized. Patents disclosing the production of terephthalic acid such as 4,158,738 and 3,996,271 are hereby incorporated by reference.

In an embodiment of this invention a process to produce purified carboxylic acid slurry **190** is provided in Figure 1. The process comprises 10 removing impurities from a crystallized product in a solid liquid displacement zone **180** to form the purified carboxylic acid slurry **190**; wherein the purified carboxylic acid slurry **190** has a b* of less than 3.5; wherein the purified carboxylic acid slurry **190** is formed without a hydrogenation step.

15 The solid liquid separation zone **180**, impurities, crystallized product **160**, and purified carboxylic acid slurry **190** are all described subsequently in this disclosure.

In another embodiment of this invention, a process to purify a staged oxidation product **110** the process comprising removing impurities from the 20 staged oxidation product **110** in a solid liquid displacement zone **180** to form a purified staged oxidation product **165**; wherein the purified staged oxidation product **165** has a b* of less than 3.5; wherein the purified staged oxidation product **165** is formed without a hydrogenation step.

The solid liquid separation zone **180**, impurities, staged oxidation product **110**, and the purified staged oxidation product **165** are all described subsequently in this disclosure.

In another embodiment of this invention a process to produce a
5 purified terephthalic acid slurry **190** is provided in Figure 1. The process comprises:

Step (a) comprises optionally removing impurities from a crude carboxylic acid slurry **30** in an optional solid liquid displacement zone **40** to form a slurry product **70**;

10 A crude carboxylic acid slurry **30** comprises at least one carboxylic acid, catalyst, at least one solvent, and impurities is withdrawn via line **30** can be at temperatures between about 110°C and about 200°C, preferably about 140°C to about 170°C from the a primary oxidation zone **20** wherein an aromatic feedstock **10**, typically paraxylene is oxidized. The impurities
15 typically comprise one or more of the following compounds: 4-carboxybenzaldehyde, trimellitic acid, and 2,6-dicarboxyfluorenone. The solvent typically comprises acetic acid, but can be any solvent that has been previously mentioned.

Generally, the crude carboxylic acid slurry **30** is produced by
20 oxidizing in a primary oxidation zone **20** an aromatic feed stock **10**. In one embodiment, the aromatic feedstock comprises paraxylene. The primary oxidation zone **20** comprises at least one oxidation reactor, and the crude

carboxylic acid slurry **30** comprises at least one carboxylic acid. Generally, the carboxylic acid is terephthalic acid.

Therefore, when terephthalic acid is utilized, the crude carboxylic acid slurry **30** would be referred to as crude terephthalic acid slurry.

5 However, suitable carboxylic acids include, but are not limited to, terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, and mixtures thereof. Crude terephthalic acid slurry is conventionally synthesized via the liquid phase oxidation of paraxylene in the presence of suitable oxidation catalyst. Suitable catalysts include, but are not limited to,
10 cobalt, manganese and bromine compounds, which are soluble in the selected solvent.

The crude carboxylic acid slurry in conduit **30** is fed to an optional solid liquid displacement zone **40** capable of removing a portion of the liquid contained in the crude carboxylic acid slurry **30** to produce the slurry product in conduit **70**. The removal of a portion of the liquid to produce a slurry product in conduit **70** can be accomplished by any means known in the art. Typically, the solid liquid displacement zone **40** comprises a solid liquid separator that is selected from the group consisting of a decanter centrifuge, rotary disk centrifuge, belt filter, rotary vacuum filter, and the like.
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20 The crude carboxylic acid slurry in conduit **30** is fed to the optional solid liquid displacement zone **40** comprising a solid liquid separator. The solid liquid separator is operated at temperatures between about 50°C to about 200°C, preferably 140°C to about 170°C and at pressures between about

30 psig to about 200 psig. The residence time can be any residence time suitable to remove a portion of the solvent and produce a slurry product in conduit **70**. The optional solid liquid separator in the optional solid liquid displacement zone **40** may be operated in continuous or batch mode,
5 although it will be appreciated that for commercial processes, the continuous mode is preferred.

The impurities are displaced from the optional solid liquid displacement zone **40** in a mother liquor and withdrawn via line **60**. Additional solvent is fed to the optional solid liquid displacement zone **40** via
10 line **50** to reslurry the crude carboxylic acid slurry **30** and form a slurry product **70**. The mother liquor is withdrawn from solid liquid displacement zone **40** via line **60** and comprises a solvent, typically acetic acid, catalyst, and bromine compounds. The mother liquor in line **60** may either be sent to a process for separating impurities from oxidation solvent from via lines not
15 shown or recycled to the catalyst system via lines not shown. One technique for impurity removal from the mother liquor commonly used in the chemical processing industry is to draw out or "purge" some portion of the recycle stream. Typically, the purge stream is simply disposed of or, if economically justified, subjected to various treatments to remove undesired
20 impurities while recovering valuable components. Examples of impurity removal processes include U.S. Patent # 4,939,297 and U.S. Patent 4,356,319, herein incorporated by reference.

Step (b) comprises oxidizing the slurry product **70** or crude carboxylic acid slurry **30** in a staged oxidation zone **80** to form a staged oxidation product **110**.

In one embodiment of the invention the slurry product **70** or crude carboxylic acid slurry **30** is withdrawn via line **70** to a staged oxidation zone **80** where it is heated to between about 190°C to about 280°C and preferably between about 200°C to about 250°C and further oxidized with air fed by line **100** to produce a staged oxidation product **110**.

The staged oxidation zone **80** comprises at least one staged oxidation reactor vessel. The crude carboxylic acid slurry **30** or slurry product **70** is fed to the staged oxidation zone **80**. The term "staged" means that the oxidation occurs in both the primary oxidation zone **20** discussed previously as well as in the staged oxidation zone **80**. For example, the staged oxidation zone **80** can comprise staged oxidation reactor vessels in series.

When the carboxylic acid is terephthalic acid, the crude carboxylic acid slurry **30** or slurry product **70** in the staged oxidation zone **80** comprises an oxidation reactor that is heated to between about 190°C to about 280°C, preferably between about 200°C to about 250°C, and most preferably between 205 °C to 225°C and further oxidized with air or a source of molecular oxygen fed by line **100** to produce a staged oxidation product **110**. Generally, oxidation in the staged oxidation zone **80** is at a higher temperature than the oxidation in the primary oxidation zone **20** to

enhance the impurity removal. The staged oxidation zone **80** can be heated directly with solvent vapor, or steam via conduit **90** or indirectly by any means known in the art. The staged oxidation zone **80** is operated at a temperature and pressure sufficient that the b* color of the staged oxidation product **110** is less than about 4. Preferably, the b* color of the staged oxidation product in conduit **110** is less than about 3.5. Most preferably, the b* color in the staged oxidation product in conduit **110** is less than about 3.

5 The b* color is one of the three-color attributes measured on a spectroscopic reflectance-based instrument. The color can be measured by any device known in the art. A Hunter Ultrascan XE instrument is typically the measuring device. Positive readings signify the degree of yellow (or absorbance of blue), while negative readings signify the degree 10 of blue (or absorbance of yellow).

Additional air or molecular oxygen may be fed via conduit **100** to the staged oxidation zone **80** in an amount necessary to oxidize a substantial portion of the partially oxidized products such as 4-carboxybenzaldehyde (4-CBA) in the crude carboxylic acid slurry **30** or slurry product **70** to the corresponding carboxylic acid. Generally, at least 70% by weight of the 4-CBA is converted to terephthalic acid in the staged oxidation zone **80**.

15 Preferably, at least 80% by weight of the 4-CBA is converted to terephthalic acid in the staged oxidation zone **80**. Significant concentrations of 4-carboxybenzaldehyde and p-toluic acid in the terephthalic acid product are particularly detrimental to polymerization processes as they act as a chain 20

terminator during the condensation reaction between terephthalic acid and ethylene glycol in the production of polyethylene terephthalate(PET).

Typical terephthalic acid product contains on a weight basis less than about 250 parts per million (ppm) 4-carboxybenzaldehyde and less than about

5 150 ppm p-toluic acid

Impurities in the crude carboxylic acid slurry **30** or slurry product **70** go into solution as terephthalic acid particles are dissolved and re-crystallized in staged oxidation zone, **80**. Offgas from the staged oxidation zone **80** is withdrawn via line **105** and fed to a recovery system where the 10 solvent is removed from the offgas comprising volatile organic compounds (VOCs). VOCs and methyl bromide may be treated, for example by incineration in a catalytic oxidation unit. The staged oxidation product **110** from the staged oxidation zone **80** is withdrawn via line **110**.

Step (c) comprises crystallizing the staged oxidation product **110** in a 15 crystallization zone **120** to form a crystallized product **160**. Generally, the crystallization zone **120** comprises at least one crystallizer. Vapor product from the crystallization zone **120** is withdrawn via line **130**, condensed in a condenser zone **150**, which comprises at least one condenser and returned to the crystallization zone **120** via conduit **140**. Optionally, the liquid in 20 conduit **140** or vapor **130** in the condenser zone **150** can be recycled, or it can be withdrawn or sent to an energy recovery device. In addition, the crystallization offgas **170** from the condenser zone **150** is removed via line **170** and can be routed to a recovery system where the solvent is removed

and crystallization offgas comprising VOCs and pollutants may be treated, for example by incineration in a catalytic oxidation unit.

When the carboxylic acid is terephthalic acid, the staged oxidation product **110** from the staged oxidation zone **80** is withdrawn via line **110** and fed to a crystallization zone **120** comprising at least one crystallizer where it is cooled to a temperature between about 110°C to about 190°C to form a crystallized product **160**, preferably to a temperature between about 140°C to about 180°C, most preferably 150°C to 170°C. The b* color of the crystallized product in conduit **160** is less than 4. Preferably, the b* color of the crystallized product in conduit **160** is less than 3.5. Most preferably, the b* color in the crystallized product in conduit **160** is less than 3.

The crystallized product **160** from the crystallization zone **120** is withdrawn via line **160**. Typically, the crystallized product **160** is then fed directly to a vessel and cooled to form a cooled crystallized product. When the carboxylic acid is terephthalic acid, the cooled crystallized product is cooled in a vessel to typically a temperature of approximately 90° C or less before being introduced into a process for recovering the terephthalic acid as a dry powder or wet cake.

In some processes prior to the present invention, the crystallized product **160** was fed directly to a flash tank. The crystallized product **160** was cooled in the flash tank to typically less than about 90°C and fed to a filtration and drying system. However, as previously stated this invention provides an attractive process to produce a purified carboxylic acid slurry by

utilizing a solid liquid displacement zone comprising a solid liquid separator at elevated temperatures after oxidation of a crude carboxylic acid slurry product and prior to final filtration and drying. The results of Examples 1 and 2 discussed subsequently clearly illustrate the significant purity
5 improvements which are achieved when the solid liquid displacement zone of the present invention is used.

Step (d) comprises removing in a solid liquid displacement zone 180 impurities from the crystallized product to form the purified terephthalic acid slurry.

10 It has been surprisingly found that when the crystallized product 160 from crystallizer zone 120 is treated in a solid liquid displacement zone 180, the purified carboxylic acid slurry 190 contains significantly less impurities, thereby improving the color of the products produced from the carboxylic acid. The solid liquid displacement zone 180 comprises a solid liquid
15 separator which includes, but is not limited to a decanter centrifuge, rotary disk pack centrifuge and other suitable solid liquid separation devices. In the embodiment where the carboxylic acid is terephthalic acid, the level of impurities in the purified carboxylic acid slurry is decreased by up to 60%. It was completely unexpected that terephthalic acid of this purity could be
20 produced utilizing the second solid liquid displacement zone 180 of the present invention without the use of a process for separating impurities from oxidation solvent as disclosed in U.S. Patent #4,939,297 or hydrogenation

as disclosed in U.S. Patent #3,584,039; both of which are herein incorporated by reference.

Thus, in one embodiment of the present invention, the crystallized product **160** is withdrawn from crystallizer zone **120** via line **160** and is fed to a solid liquid displacement zone **180** comprising a solid liquid separator to produce a purified carboxylic acid slurry in conduit **190**. The solid liquid displacement zone **180** comprises a solid liquid separator. In one embodiment of the invention the solid liquid separator can be operated at temperatures between about 50 °C to about 200 °C, another range is the solid liquid separator can be operated at 110 °C to 200 °C, preferably between about 120 °C to about 180 °C, and more preferably between about 140 °C to about 160 °C and at pressures above the flash point for the selected solvent. For the case where the solvent is acetic acid, the pressure is generally less than 200 psia. The solid liquid separator in the second solid liquid displacement zone **180** may be operated in continuous or batch mode, although it will be appreciated that for commercial processes the continuous mode is preferred.

The impurities are displaced from the solid liquid displacement zone **180** in a mother liquor stream and withdrawn via line **185**. Additional solvent is fed to the solid liquid displacement zone **180** via line **183** to reslurry the crystallized product and form the purified terephthalic acid slurry. The purified carboxylic acid slurry is withdrawn from displacement zone **180**, via line **190**. Optionally, the purified carboxylic acid slurry in

conduit **190** can then be fed to a flash tank and flash cooled to less than about 90 °C.

In other embodiments of this invention, the solid liquid displacement zone **180** can be located after the staged oxidation zone **80** as shown in 5 Figure 2. Even though the process zones are located in a different order, the function of the zones are the same as previously described. Impurities are displaced from the feed stream from the solid liquid displacement zone **180** via line **185**. The feed stream to the solid displacement zone **180** is the staged oxidation product **110**. When the feed stream to the solid liquid 10 displacement zone **180** is a staged oxidation product **110** a purified staged oxidation product **165** is produced. The impurities are displaced from the solid liquid displacement zone **180** in a mother liquor stream and withdrawn via line **185**.

The mother liquor stream **185** comprises carboxylic acid, water, a 15 solvent, suitable oxidation catalyst(s) and bromine compounds and corrosion metals. The bromine compounds are used as promoters in the oxidation reaction. Examples of corrosion metals are iron and chromium compounds, which inhibit, reduce or entirely destroy the activity of the suitable oxidation catalyst. Suitable carboxylic acids are selected from the 20 group consisting of terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, and mixtures thereof. Additional solvent is fed to the solid liquid displacement zone **180** via line **183** to reslurry the crystallized product and form the purified terephthalic acid slurry. The purified carboxylic acid

slurry is withdrawn from the solid liquid displacement zone 180, via line 190.

Optionally, the purified carboxylic acid slurry in conduit 190 can then be fed to a flash tank and flashed cooled to less than about 90 °C.

It should be appreciated that the process zones previously described
5 can be utilized in any other logical order. It should also be appreciated that when the process zones are reordered that the process conditions may change.

In another embodiment of this invention each embodiment can
10 optionally include an additional step comprising decolorizing the carboxylic acid or an esterified carboxylic acid via hydrotreatment.

The decolorizing of the purified carboxylic acid slurry or an esterified carboxylic acid can be accomplished by any means known in the art and is not limited to hydrogenation. However, for example in one embodiment of the invention, the decolorizing can be accomplished by reacting a
15 carboxylic acid that has undergone esterification treatment , for example with ethylene glycol, with molecular hydrogen in the presence of a catalyst in a reactor zone to produce a decolorized carboxylic acid solution or a decolorized ester product. For the reactor zone, there are no special limitations in the form or construction thereof, subject to an arrangement
20 that allows supply of hydrogen to effect intimate contact of the carboxylic acid or ester product with the catalyst in the reactor zone. Typically, the catalyst is usually a single Group VIII metal or combination of Group VIII metals. Preferably, the catalyst is selected from a group consisting of

palladium, ruthenium, rhodium and combination thereof. The reactor zone comprises a hydrogenation reactor that operates at a temperature and pressure sufficient to hydrogenate a portion of the characteristically yellow compounds to colorless derivatives

EXAMPLES

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these 5 examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

Comparative Example 1

Paraxylene was oxidized at 160°C utilizing a Co, Mn, Br catalyst 10 system to produce a crude terephthalic acid slurry having 30-35% solids. The crude terephthalic acid slurry was crystallized and purified using the process shown in Figure 1 with the omission of Zone **180** and the 15 crystallized product from the crystallization zone **120** was transferred directly to flash tank. The product was removed after filtration and drying and analyzed for 4-CBA, TMA, 2,6-DCF, percent transmittance and b*. The b* is one of the three-color attributes measured on a spectroscopic 20 reflectance-based instrument. A Hunter Ultrascan XE instrument is typically the measuring device. Positive readings signify the degree of yellow (or absorbance of blue), while negative readings signify the degree of blue (or absorbance of yellow).

The concentration of 4-CBA, TMA, 2,6-DCF in the terephthalic acid were analyzed via liquid chromatography. To determine the percent transmittance, a 10% solution of terephthalic acid product in 2M KOH was

measured using a UV visible spectrometer at 340nm. The b* of the terephthalic acid was measured using a reflectance color method at 340nm. The results are shown in Table 1.

5 Inventive Example 2

Example 1 was repeated except that the crystallized product from the crystallization zone 120 was fed to a solid liquid separation zone 180 comprising a rotary disk centrifuge at a temperature of 155°C and the solvent wash was fed to the rotary disk centrifuge at a temperature of 10 145°C. The purified terephthalic acid product was collected and analyzed as in Example 1. The results are shown in Table 1.

Table 1

Ex. #	4-CBA ¹ (ppm)	TMA ² (ppm)	2,6-DCF ³ (ppm)	%T ⁴	b* ⁵
1	103	51	10	89	4.1
2	44	23	4	95	2.9

15 ¹4-CBA is 4-carboxybenzaldehyde

²TMA is trimellitic acid

³2,6-DCF is 2,6-dicarboxyfluorenone

⁴%T is % transmittance at 340 nm

⁵b* is a measure of yellow-blue color

The results of Examples 1 and 2 clearly illustrate the significant purity improvements which are achieved when the solid liquid displacement zone of the present invention is used. The amount of impurities present in 5 the purified terephthalic acid product produced by the process of the present invention decreased between about 50 and about 60%. The % transmittance of the purified terephthalic acid product has a direct influence on the color of the polyethylene terephthalate (PET) produced. Desirable PTA (purified terephthalic acid) is white (which is referred to as having low 10 color). Higher % transmittance indicates less color in the PTA. The human eye can detect 0.5 differences in b^* . Thus, the 1.2 difference between the non-hydrogenation process (Example 1) which displays a b^* of greater than about 4, and the process of the present invention (Example 2) which shows a b^* less than about 3 represents a very noticeable decrease in the 15 yellowness of the terephthalic acid slurry. The degree of improvement in all the measured categories is particularly surprising given the simplicity of the centrifugation in the solid liquid separation zone 180. In the past, comparable purity levels have been achieved only by utilization of a hydrogenation plant which includes numerous steps and pieces of 20 equipment, and significant capital investment.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations

and modifications can be effected within the spirit and scope of the invention.